

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)

31/01/02

2. REPORT DATE

FINAL REPORT

3. DATES COVERED (From - To)

7/1/96-9/30/01

4. TITLE AND SUBTITLE

Solid Freeform Fabrication from Gas Precursors
Using Laser Processing

5a. CONTRACT NUMBER

N00014-95-1-0978

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)

Marcus, Harris L.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Institute of Materials Science, UConn
97 N. Eaglevill Rd., Unite 3136
Storrs, CT 06269-3136

8. PERFORMING ORGANIZATION
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Ralph Wachter
ONR
800 N. Quincy St., Arlington, VA 22217-5660

10. SPONSOR/MONITOR'S ACRONYM(S)

ONR

12. DISTRIBUTION AVAILABILITY STATEMENT

Distribution Unlimited

20020627 117

13. SUPPLEMENTARY NOTES

Final Report sent to ONR (Wachter) 31/01/02 & web site www.ims.uconn.edu/metal/faculty/marcus.htm

14. ABSTRACT

The objective of the research was to establish the technical approaches required to use localized laser induced chemical vapor deposition as an approach for solid freeform fabrication (SFF). The Three processing approaches to be developed are Selective Area Laser Deposition (SALD), Selective Area Laser Deposition Vapor Infiltration (SALDVI), and Selective Area Laser Deposition Joining (SALD-Joining) of ceramics.

15. SUBJECT TERMS

Solid Freeform Fabrication (SFF), Selective Area Laser Deposition (SALD), Selective Area Laser Deposition Vapor Infiltration (SALDVI) and Selective Area Laser Deposition Joing (SALD-Joining)

16. SECURITY CLASSIFICATION OF:

a. REPORT

b. ABSTRACT

c. THIS PAGE

17. LIMITATION OF
ABSTRACT

18. NUMBER
OF PAGES

19a. NAME OF RESPONSIBLE PERSON

19b. TELEPHONE NUMBER (Include area code)

Solid Freeform Fabrication from Gas Precursors Using Laser Processing
Final Report, 1996-2001

Principal/co-Principal Investigator.

- * PI/co-PI Name(s): Harris L. Marcus, co-PI Leon Shaw
 - * PI Institution: University of Connecticut, Storrs
 - * PI Phone Number: (860) 486-4623
 - * PI Fax Number: (860) 486-4745
 - * PI Street Address: 97 North Eagleville Road
 - * PI City, State, Zip: Storrs, CT 06269-3136
 - * PI E-mail Address: hmarcus@mail.ims.uconn.edu
 - * PI URL Home Page: <http://www.ims.uconn.edu/metal/faculty/marcus.htm>
 - * Grant/Contract Number: N00014-95-1-0978
 - * Period of Performance: 07/01/96 - 9/30/01
-

Productivity Measures.

- * Number of refereed papers submitted not yet published: 1
- * Number of refereed papers published: 11
- * Number of unrefereed reports and articles: 30
- * Number of books or parts thereof submitted but not published:
- * Number of books or parts thereof published: 2
- * Number of project presentations: 40
- * Number of patents filed but not yet granted:
- * Number of patents granted and software copyrights: 2(From U. of Texas work)
- * Number of graduate students supported \geq 25% of full time: 6
- * Number of post-docs supported \geq 25% of full time: 1
- * Number of minorities supported: 3

Objective of Research

The objective of the research was to establish the technical approaches required to use localized laser induced chemical vapor deposition as an approach for solid freeform fabrication (SFF). The three processing approaches to be developed are Selective Area Laser Deposition (SALD), Selective Area Laser Deposition Vapor Infiltration (SALDVI), and Selective Area Laser Deposition Joining (SALD-Joining) of ceramics.

Executive Summary

In this overall final report on the research into the three processing approaches, Selective Area Laser Deposition (SALD), Selective Area Laser Deposition Vapor Infiltration (SALDVI), and Selective Area Laser Deposition Joining (SALD-Joining) of ceramics only limited details are included. The reader can get greater detail in the over forty publications listed below that resulted from this research.

In terms of producing SFF shapes the SALDVI was the most successful. It was used to produce simple geometric parts of SiC or Si₃N₄ into SiC, Si₃N₄, metal and other powders. One of the more successful composites made was SiC deposited into Mo powder. The advantage of the layer by layer infiltration technique was clearly shown. The primary difficulties in the SALDVI processing were prevention of SALD overlay onto each layer, some residual porosity, and the very slow processing rate. The approach was characterized for the different materials in terms of laser power, scanning rate, preheat temperature, precursor gas pressure, precursor gases, raster geometry, line overlap, and laser wavelength, primarily using Nd:YAG and CO₂ lasers. As part of the effort finite element calculations of the processing parameters were made to help define the appropriate processing space.

To demonstrate the use of SALD and SALDVI together devices buried in a bulk material were produced. The most successful were C/SiC embedded thermocouples. This used SALDVI to produce the bulk SiC, SALD to coat the bulk SiC with Si₃N₄ as an insulator followed by SALD deposition of the C and SiC legs of the thermocouple. The thermocouple was then sealed with another SALD layer of Si₃N₄ and finally encapsulated in the multiple layers of SALDVI SiC. Samples with multiple thermocouples were also produced and demonstrated. This showed the wide potential of the combined SALD/SALDVI processing.

The third approach of SALD joining was fully demonstrated. SALD deposition of SiC deposited from the tetramethylsilane gas precursor joined two pieces of SiC. Similar results were obtained for Si₃N₄. This ability to "weld" ceramics with the same material to be joined has great promise. The primary difficulty is associated with the limited throwing power of the approach due to the surface being hotter than the inside of any joint geometry used.

A Solid Freeform Fabrication laboratory was designed and assembled, with a starting point of an empty room. Three unique and fully functional computer controlled gas phase laser-based SFF systems are presently in place. Overall the SALD, SALDVI and SALD Joining were all demonstrated and many of the processing parameters worked

out. The potential availability of gas precursors for most materials makes them potentially a very strong possibility for SFF of many complex materials. Overall there will be a great deal of additional effort necessary to make the processes robust.

Summary of Technical Progress.

Equipment

A Solid Freeform Fabrication laboratory was designed and assembled, with three SFF systems presently in place. Two systems have Powder Delivery System (PDS) units for spreading out a powder substrate, necessary for the SALDVI process. One system offers a four inch by four and a half inch target area for large part production, while the other system has a one inch diameter target area. The third system is used for SALD/SALD joining and contains a SALD joining machine, incorporating a variable speed rotational device designed to work with tube structures. The large PDS sits in a 28 inch diameter, 15 inch tall vacuum system with a double-walled cooling jacket. The two other systems are eight inch diameter, eight inch tall vacuum chambers that have been nickel-plated to protect against the corrosive environments of some precursors and reaction by-products. Two in-situ chemical analysis tools have been implemented into the SALD/SALDVI systems. The first is a residual gas analyzer, and the second is a four point sampling emission spectrometer.

Five lasers are operational, 25 and 50 watt continuous wave CO₂ (10.6 micron wavelength), 50 and 150 watt Nd:YAG (1.064 micron wavelength), and a 6 watt harmonic generating pulsed Nd:YAG (1.064, .532, .355, .266 micron wavelengths at the fundamental and 2nd, 3rd, and 4th harmonic wavelengths, respectively). X-Y translational equipment, optics, electronic components, three computers and associated software are all utilized in laser scanning. Ancillary laboratory equipment needed for proper laboratory procedures and safety has also been acquired and put to use, including a glove box for liquid precursor handling, a micron filter vacuum for powder cleanup, and compressed gas cylinder equipment.

An integrated temperature closed loop and scanning motion control computer program has been designed and refined in-house for the SFF systems. The program was written in Visual Basic. The closed loop uses the output from an emissivity-measuring infrared pyrometer to monitor temperature at the reaction zone of the laser beam. The program compares this readout to a user-defined temperature and makes adjustments in laser power by altering the input voltage to the laser controller with an analog voltage output card. Concurrent with this operation, the Visual Basic program directs the motion control hardware. Custom motion programs can be designed and inputted into the program. Data acquisition of the processing parameters such as laser power, pyrometer temperature and emissivity, and other signals is included. These processing control programs also have the capability to generate 2-D scan patterns automatically from 3-D computer geometrical models.

Technical Results

The specific research programs at the UCONN SFF lab focus on ceramic fabrication from the gas-phase reactions. Fundamental understanding of the SALD and SALDVI processes are essential to applying the technology to real world applications.

The results below are summaries of technical progress in the three SALD research areas. For greater details, the reader is referred to the relevant publications.

SALDVI

The SALDVI work is focused on fabricating SiC bulk shapes by infiltration of SiC powder particles with vapor deposited SiC derived from tetramethylsilane (TMS) gas, although other starting powders (carbides, nitrides, oxides, metals) were also investigated. Powders of different size were mixed to vary the packing fraction and surface area. Laser scanning was performed using a range of gas precursor pressures using different temperature distributions and local heating times. Quantitative metallography was used to measure the variations in the amount of infiltration with position in the samples for each powder and processing condition. A comparison of the measured infiltration profiles shows that the properties of the starting powder influence the vapor infiltration in the powder layer. The variations in the measured infiltration profiles were analyzed and correlated with the variations in the physical properties of the starting powders to obtain a general predictive model of the process. The results show that solid density of more than 90 percent can be obtained in a region within 250 microns of the free surface of the powder layer under certain processing conditions. Process control was enhanced to allow automatic control of the heating and cooling rate whenever the laser beam is turned on or off. The capability to preheat the powder bed and SALDVI workpiece was also added.

The feasibility of fabricating SiC cermets by SALDVI was investigated, particularly by combining vapor deposited SiC with copper, molybdenum, and nickel powder layers. The microstructures of the three SALDVI cermets reveal varying degrees of reactions between the metal powders and the vapor deposited SiC matrix. Both the Cu and Ni powders react with vapor deposited SiC during the SALDVI process at all of the processing temperatures (1000-1200 C) and heating times (200-800 s) examined here. For the Cu powder, particles at least 20 μm in diameter had reacted to form a Cu silicide phase even at the shortest heating time of 200 s and lowest processing temperature of 1000 C. Further evidence of Cu silicide formation was observed in x-ray diffraction measurements at 1000 and 1200 C target temperatures. These results indicate that Si is a fast diffuser in Cu. In the Ni case, the extent of the reactions progressed more notably with increasing processing temperature and heating duration. X-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS) measurements indicate the formation of the Ni_2Si phase, as well as additional phases not yet identified. For the Mo/SiC cermet, no Mo-Si interdiffusion was detected by XRD or EDS for the 1000 C target temperature. This is not surprising as the melting temperature of Mo is 2610 C, so diffusion would be expected to occur slowly at 1000 C. The Mo/SiC cermet shows the highest bending strength of 50 MPa of the three cermets. This behavior is attributed to the close thermal expansion match between the two materials resulting in few particle debonds compared to the Cu and Ni cases. Figure 1 shows a typical as-fabricated single line, three layer, 20 mm long SALDVI Mo/SiC cermet (a) and a SEM image of a polished cross-section through its centerline region (b). The Mo particles appear well bonded to the SiC matrix and the solid density exceeds 95 % in this region, as measured by quantitative metallography.

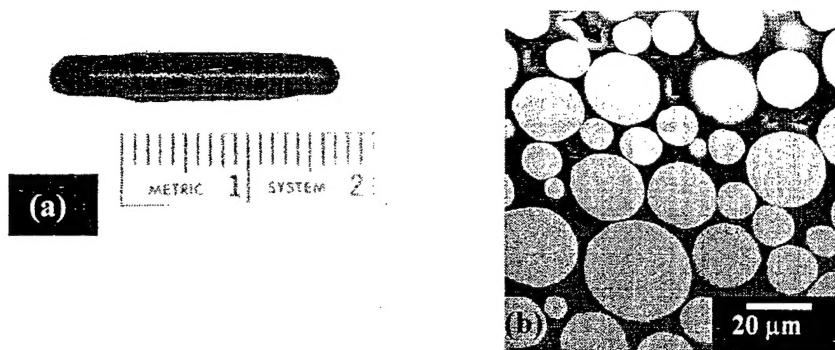


Figure 1. As-fabricated three layer, single line macrostructure (a) and SEM image of the microstructure of Mo/SiC SALDVI cermet.

The role of the starting powder on the development of the final SALDVI structure was also investigated. Silicon carbide was deposited by SALDVI from the gas precursor tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, into loosely packed powder layers of SiC, ZrO_2 , WC or Mo. Layered samples were fabricated for each powder material using both single line (bar) and multiple line (rectangle) laser scan patterns and 10 Torr $\text{Si}(\text{CH}_3)_4$, 2.5 $\mu\text{m/s}$ scan speed, 1000°C target temperature, and 120 μm layer thickness. Samples of SiC and ZrO_2 are prone to surface cracking in the bar geometry, and cracking and delamination of layers in the rectangle geometry. Samples fabricated with Mo powder have no cracks or delamination defects in either bar or rectangle geometry as well as a better surface appearance. Figure 2 shows a Mo powder/SiC matrix rectangle with 6 layers (a) as-fabricated and (b) cross-section across layers. Thermal stress plays a major role in cracking in bar and rectangle samples of SiC matrix/SiC powder and SiC matrix/ ZrO_2 powder made by SALDVI. The effective thermal conductivity (k_{eff}) of the SALDVI workpiece correlates well with the severity of thermal cracking. The lower k_{eff} the more severe the cracking. SiC matrix/Mo powder samples have the highest k_{eff} , and show no cracking. The irregular shape of the SiC and ZrO_2 powders, as well as a higher surface roughness, could provide stress risers in the matrix during processing, increasing their susceptibility to thermal cracking compared to the spherical Mo powder. The type of powder was found to affect the surface appearance and internal structure of SiC matrix multiple layer SALDVI rectangles. Samples with SiC and ZrO_2 powder show a porous surface appearance due to displacement of the powder during processing. Mo and WC powder samples have a dense surface and continuous solid material across adjacent layers. The lower density of the SiC and ZrO_2 powders and convective effects in the gas are the likely cause of their poor structure and rough surface appearance.

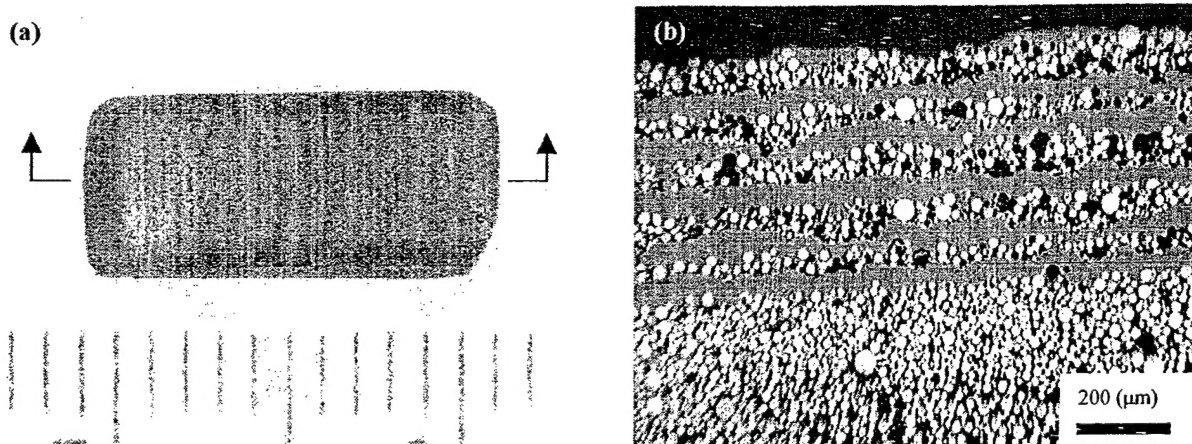


Figure 2. Mo powder/SiC matrix rectangle with 6 layers (a) as-fabricated and (b) cross-section across layers.

A 3D finite element model was also developed to simulate the SALDVI of silicon carbide. The model predicts the laser input power and the distribution of vapor deposited SiC within the powder bed as well as on the surface of the powder bed (SALD). The model includes closed-loop control of the laser power to achieve a desired target processing temperature on the top surface of the powder bed. This model considers a moving Gaussian distribution laser beam, temperature- and porous-dependent thermal conductivity, specific heat and temperature-dependent deposition rate. A schematic of the model is shown in Figure 3. The simulation results compare well with experimental data as shown in Figure 4.

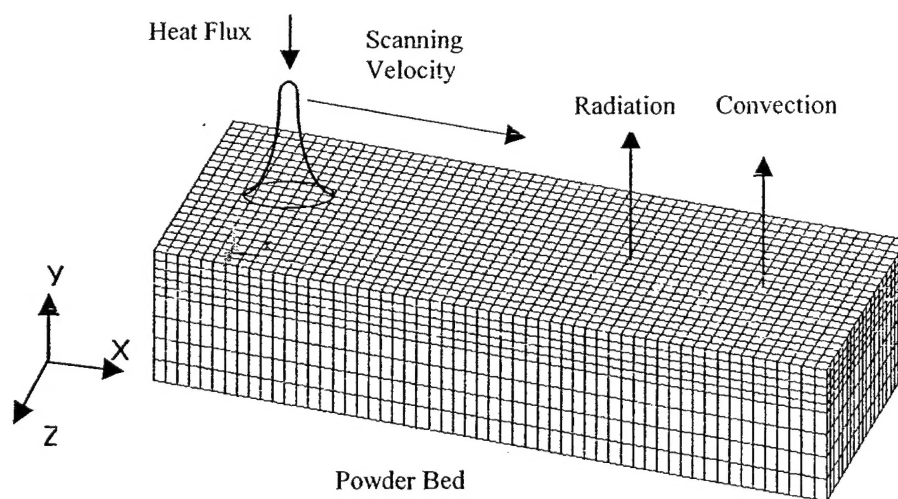


Figure 3. Finite element model of the SALDVI process.

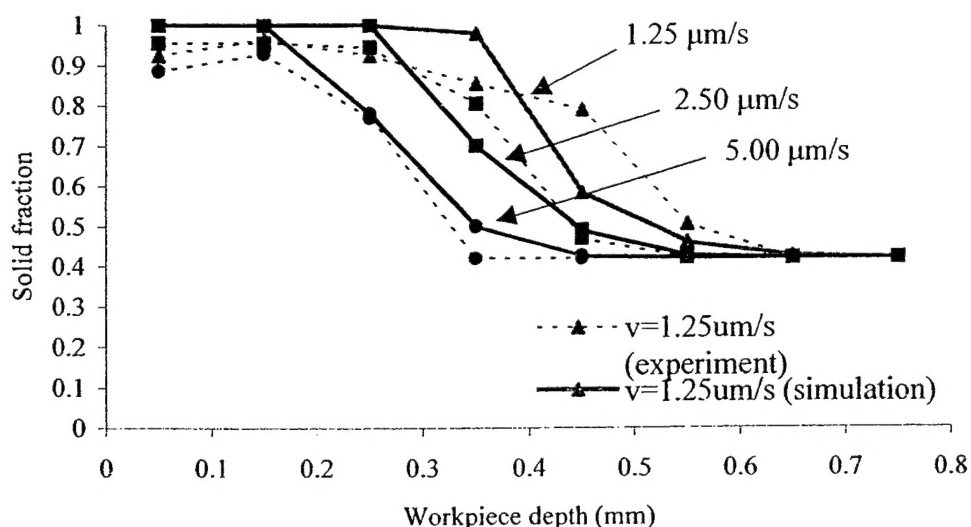


Figure 4. Comparison between the experimental and simulated solid fraction distribution in depth direction under the center of the laser beam after the scanning process at $x=7$ mm.

The simulation results of the incident laser power history and the distribution of vapor infiltrated SiC in the powder bed agree fairly well with the experiments. As the laser scanning rate decreases, the incident laser power increases. As the laser scanning rate decreases, the deposition of SiC both within the powder bed as well as on the surface of the powder bed (SALD) increases (Figure 4). Uniform temperature on the top surface of powder bed during laser scanning process needs non-uniform laser power at the initial scanning period and nearly uniform laser power elsewhere. These simulation results offer guidelines for further experimental studies of the SALDVI process.

SALD and integrated SALD/SALDVI

SALD research looked at multiple material deposition. Specifically, silicon nitride, from TMS and ammonia, and silicon carbide and carbon, from TMS and acetylene respectively, were examined. The silicon nitride was deposited as a thin film, and analyzed with respect to its insulative quality. The deposition was performed at low ammonia pressures, approximately 10 to 20 torr, using a carbon dioxide laser. The successful formation of the nitride layer countered previous notions of not being able to use ammonia gas precursors with a CO_2 laser. Silicon carbide and carbon were deposited in line formations, with the resulting electrical properties coming under scrutiny. The line resistances and emf response to temperature changes were tested with respect to varied line widths (a function of scan speed and laser beam size) and deposition temperature field. These SALD/SALDVI investigations were applied to an embedded sensor project sponsored by DARPA. The DARPA program studied the feasibility to fabricate a ceramic matrix with an operational, in-situ thermocouple formed inside the matrix structure in one continuous process. An example of a SALD/SALDVI silicon carbide/carbon thermocouple in a silicon carbide matrix, along with its temperature and emf response, can be found at the UCONN website.

It was found that the experimental results are in excellent agreement with the theoretical thermodynamic predictions. With the use of acetylene (C_2H_2), tetramethylsilane (TMS), and a mixture of TMS and ammonia, graphite, SiC, and Si_3N_4 were successfully deposited, respectively. Strong temperature dependency of the SALD products in morphology, composition, crystal structure and size, growth kinetics and relevant properties were revealed. The predicted carbon co-deposition and the role of hydrogen gas in eliminating this co-deposition in SiC or Si_3N_4 were experimentally confirmed by a Raman scattering study. The functional test on the fabricated device showed that the embedded SiC/C thermocouples exhibited stable and repeatable response to temperature variations. Thus, the overall results indicated that it is feasible to embed the in-situ sensors within a ceramic matrix using the combined SALD/SALDVI techniques.

SALD-Joining

Another area of investigation in the SFF laboratory is ceramic joining by SALD, a patented process for substrate-involved SALD deposition. The joining of ceramic parts is accomplished by using a filler material deposited from the gas-phase reaction in SALD. In this manner, the ceramic joint can be tailored to match the material composition of the constituent ceramic part to be joined. The initial efforts focused on joining clay-bonded silicon carbide (approximate 75 to 80% density) tubes with silicon carbide deposited from TMS precursor. The adhesion of the SALD material to the tube is excellent. In fact, the interface between the SALD material and the tube is inconspicuous. The success of joints in this initial phase has been inconsistent. While the adhesion is outstanding, successful connective bonding of the SALD material across the joint has been challenging. An example of two clay-bonded silicon carbide tubes connected by the SALD joining method can be found at the UCONN website.

Investigation on this project has yielded several successfully joined silicon carbide tube structures using silicon carbide deposited filler from the gas-phase pyrolysis of tetramethylsilane. Adhesion of the deposit to the tube surface remains excellent. Bend testing of joined samples produced poor strength values, likely due to the butt-end nature of the joint geometry. This leaves an existing 'crack' at the joint seam the length of the tube wall. Beveling of the tube ends has become a central focus to achieve stronger joints, not only to reduce the initial crack length but to also increase the surface area of tube/deposit adhesion interface. The hermetic quality of the several joints was examined, compared to a monolithic standard of the base tube used. The SALD joints held a steady-state vacuum (in Torr) within a factor of 10 of the vacuum held by the standard. Improvements in the deposit morphology, from a billowy, porous nature to a more laminar deposition, are expected to improve these hermeticity values.

Preheating the silicon carbide substrate during the SALD deposition process is a controlling parameter for producing high density, high purity, defect-reduced silicon carbide filler. The preheating reduces the thermal gradient occurring during the joining process. SALD tube joint structures show greatly reduced mechanical bend strengths compared to monolithic tube standards. The origins for the lower strength are the initial crack found at the joint seam of the butt-end tube configuration and the reduction in the cross-sectional area of the SALD filler deposit compared to the full tube cross-sectional area due to the poor 'throwing power' of the laser associated with localized CVD. The

SALD gas-phase decomposition of tetramethylsilane, with and without hydrogen, deposits nano-crystalline silicon carbide. Characterization of the SALD silicon carbide filler material shows deviations from the expected beta-polytype in the XRD, NMR and TEM patterns that are attributed to twinning faults. This is the first evidence of twins in SALD silicon carbide but is consistent with the very low stacking fault energy for silicon carbide.

Transitions and DOD Interactions.

Briefing on SFF applications to future naval operations to Fellows of the Chief of Naval Operations' Strategic Studies Group, Capt. T.D. Glass USN, Capt. D.R. Ellison USN, and LCDR S.L. Kruppa USN, at Newport, RI April, 1996

Presentation on "Laser Solid Freeform Fabrication: SLS, SALD, SALDVI" at the ONR review meeting in Woods Hole, MA, May 29th-30th, 1996

Presentation on "Solid Freeform Fabrication at the University of Connecticut" at the ONR annual review meeting in Woods Hole, MA, June 16th, 1997

Presentation of research programs and tour of the SFF laboratory for Dr. William Coblenz of DARPA, August 8th, 1997

Dr. Marcus took a 4 day trip on the USS Tunney submarine from San Diego, CA to Seattle, WA, September, 1997

Briefing on SFF at Navy War College, Newport, RI, 1998.

Sustained contacts and interactions with Bettis and Knowles Atomic Power Laboratory on SALD, SALDVI, and SALD joining of ceramics.

Presentations on SALD SFF techniques to Carderock Division of NSWC, 2000.

Software and Hardware Prototypes.

1. Prototype Name: SALD and SALDVI System Prototypes

+ URL:

+ Availability: Available in SFF laboratory, Institute of Materials Science, UCONN

+ Description: Hardware and software of performing gas phase SFF of structures and infiltration of powder layers.

Invited Presentations

Presentations on "Selective Area Laser Deposition: A Gas Phase Solid Freeform Fabrication Approach" and "Solid Freeform Fabrication Processing Using Gas Phase Approaches" at the ASM/TMS Materials Week conference, Cleveland, OH, October 30th-November 2nd, 1995

Presentation on "Solid Freeform Fabrication Using Powder and Gas Precursors" at the Dept. of Mechanical Engineering, Aeronautical Engineering and Mechanics Colloquium series, Rensselaer Polytechnic Institute, November 17th, 1995

Presentation on "Solid Freeform Fabrication" at the Institute of Materials Science Associate Program Annual Meeting, University of Connecticut, May 23rd, 1996

Presentation on "Solid Freeform Fabrication at The University of Connecticut" at the Solid Freeform Fabrication Symposium at The University of Texas at Austin, August 12th-14th, 1996

Presentation on "Solid Freeform Fabrication of Powders Using Laser Processing" at the PM2TEC conference, Washington, D.C., June 19th, 1996

Presentation on "Solid Freeform Fabrication of Ceramics" at the Society of Manufacturing Engineers conference, Newton, MA, October 23rd, 1996

Presentation on "Solid Freeform Fabrication: An Overview" at the ASME/MED Symposium on Rapid Response Manufacturing, Atlanta, GA, November, 1996

"Recent Advances in SALD and SALDVI," Seventh International Conference on Rapid Prototyping 1997, San Francisco, March 31-April 3, 1997

"Gas Phase Solid Freeform Fabrication at the University of Connecticut," MRS Annual Meeting, Solid Freeform Fabrication Session, San Francisco, March 31 - April 4, 1997

"Selective Area Laser Deposition (SALD) of Titanium Oxide," 6th European Conference on Rapid Prototyping and Manufacturing 1997, Nottingham, UK, July 1-3, 1997

Solid Freeform Fabrication Symposium 1997, Austin, TX, August 11-13, 1997, 4 presentations on the following topics: a) The Use of VRML to Integrate Design and Solid Freeform Fabrication, b) Gas Phase SFF Control System for Silicon Nitride Deposition by SALD/SALDVI, c) Fabrication of In-Situ SiC/C Thermocouples by Selective Area Laser Deposition, d) Net Shape Functional Parts Using Diode Laser

"Selective Area Laser Deposition Joining of Silicon Carbide," American Ceramic Society 1997 Fall Meeting, San Francisco, October 12-15, 1997

Workshop on Layered Manufacturing, Oxford, England, June, 1998, Invited Speaker

"Gas-Phase Selective Area Laser Deposition (SALD) Joining of SiC Tubes with SiC Filler Material", 1998 Solid Freeform Fabrication Symposium, August 10th-12th, 1998, Austin, TX

"Preparation and Properties of In-Situ Devices Using the SALD and SALDVI Techniques", 1998 Solid Freeform Fabrication Symposium, August 10th-12th, 1998, Austin, TX

"Properties of SiC/C Thermocouple Device Made with SALD and SALDVI Techniques", 1998 American Ceramic Society Meeting, May 3rd-May 6th, 1998, Cincinnati, OH

"Selective Area Laser Deposition of Silicon Nitride", 1998 American Ceramic Society Meeting, May 3rd-May 6th, 1998, Cincinnati, OH

Patents issued to Principal Investigator

Selective Laser Sintering using Nanocomposite Materials, Ram Manthiram, David Bourell and Harris L. Marcus, Patent # 5,431,967, July 11, 1995

Joining Ceramics and Attaching Fasteners to Ceramics by Gas Phase Selective Beam Deposition, James V. Tompkins, Britton R. Birmingham, Kevin J. Jakubenas and Harris L. Marcus, Patent #5,611,883, March 18, 1997

List of Publications:

"Solid Freeform Fabrication at The University of Connecticut" by S. Harrison, J.E. Crocker, T. Manzur, and H.L. Marcus, *Proceedings of the 1996 Solid Freeform Fabrication Symposium*, Austin, TX, August 1996, 345-348.

Abstract: Gas phase solid freeform fabrication research at The University of Connecticut focuses on two main procedures, Selective Area Laser Deposition (SALD) and Selective Area Laser Deposition Vapor Infiltration (SALDVI). A SFF research laboratory is under construction at UCONN, with two new operation systems. These systems possess temperature control, data acquisition capabilities, in-situ video monitoring, and the ability to fabricate SALDVI parts up to four inches wide by four inches long. The procurement of a harmonic generating Nd:YAG six watt laser, capable of producing output at 532, 355, and 266 nanometer wavelengths, as well as a coupled effort with the Photonics Center at the University providing laser diodes at a variety of wavelengths, presents the opportunity to explore interactions involved in gas reactions driven by lasers. Investigations of material systems will include ceramic carbides, nitrides, and their composites, as well as metals.

"Solid Freeform Fabrication: An Overview" by H.L. Marcus, S. Harrison, and J.E. Crocker, *Proceedings of the Symposium on Rapid Response Manufacturing 1996*, Atlanta, GA, Nov. 17-22, 1996. **Abstract:** Solid Freeform Fabrication (SFF) has become a prominent area of interest and research in the last 10 years. SFF produces parts directly through additive procedures, without any part-specific tooling. The design for the part originates in a Computer Aided Design (CAD) file which is a three dimensional representation of the part that is sectioned into thin two dimensional layers from which the part is built. SFF vastly enhanced the prototype production process, and now looks to make advances for short run productions and tool and dies. This paper presents an overview of SFF, in terms of where it has been, what it is today, and where it will go in the future.

"Recent Advances in SALD and SALDVI", by K. Jakubenas, B.R. Birmingham, S. Harrison, J.E. Crocker, J. Sanchez, and H.L. Marcus, *Proceedings of the Seventh International Conference on Rapid Prototyping 1997*.

"Current and Future Trends in Solid Freeform Fabrication", by D.L. Bourell, J.J. Beaman, J.W. Barlow, R.H. Crawford, H.L. Marcus, and L.E. Weiss, *SPIE Proceedings Volume 2910*, Rapid Product Development Technologies, Boston, MA, November, 1996.

"Selective Area Laser Deposition (SALD) of Titanium Oxide" by K.J. Jakubenas, Y.L. Lee, M.S. Shaarawi, H.L. Marcus, and J.M. Sanchez, *Proceedings of the 6th European Conference on Rapid Prototyping and Manufacturing 1997*, edited by P.M. Dickens, University of Nottingham, p. 119-126.

"Selective Area Laser Deposition of Titanium Oxide" by K.J. Jakubenas, Y.L. Lee, M.S. Shaarawi, H.L. Marcus, and J.M. Sanchez, *Rapid Prototyping Journal*, Vol. 3, No. 2, 1997, p. 66-70.

"Recent Advances in SALD and SALDVI", by K. Jakubenas, B.R. Birmingham, S. Harrison, J.E. Crocker, J. Sanchez, and H.L. Marcus, *Proceedings of the Seventh International Conference on Rapid Prototyping 1997*, edited by R.P. Chartoff, A.J. Lightman, M.K. Agarwala, and F. Prinz, University of Dayton, p. 60-69.

"The Use of VRML to Integrate Design and Solid Freeform Fabrication", by Y. Wang, J. Dong, and H.L. Marcus, *Proceedings from the 1997 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1997, 669-676. **Abstract:** The Virtual Reality Modeling Language (VRML) was created to put interconnected 3D worlds onto every desktop. The 3D VRML format has the potential for 3D fax and Tele-Manufacture. An architecture and methodology of using VRML format to integrate a 3D model and Solid Freeform Fabrication system are described in this paper. The prototype software discussed in this paper demonstrates the use of VRML for Solid Freeform Fabrication process planning. The path used from design to part will be described.

"Fabrication of In-Situ SiC/C Thermocouples by Selective Area Laser Deposition", by L. Sun, K.J. Jakubenas, J.E. Crocker, S. Harrison, L.L. Shaw, and H.L. Marcus, *Proceedings from the 1997 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1997, 481-488. **Abstract:** With the intrinsic nature to process small features, selective area laser deposition (SALD) is a potential technique to fabricate complex shaped macro-components with in-situ high-resolution micro-devices. In the study, SALD was used to deposit in-situ SiC/C thermocouples on

alumina and silicon carbide substrates with a CO₂ laser. Tetramethylsilane (TMS) and acetylene (C₂H₂) were chosen as precursors for deposition of the silicon carbide and carbon lines respectively. The electromotive force (emf) of the deposited thermocouple was measured and found to respond sensitively to temperature variations from room temperature to 800 °C. The effect of the deposition parameters on the product morphology was also investigated with the SEM.

"Gas Phase SFF Control System for Silicon Nitride Deposition by SALD/SALDVI", by S. Harrison, C.F. Costa, K.J. Jakubenas, J.E. Crocker, and H.L. Marcus, *Proceedings from the 1997 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1997, 241-246. **Abstract:** A closed-loop laser scanning and temperature control system has been developed for SALD/SALDVI. Temperature control is especially important in SALD/SALDVI because temperature plays a defining role in both composition and deposition rate. The control system for SALD/SALDVI is presented which provides .STL file interpretation, real time temperature control, and laser response modeling, all on a PC. This control system was utilized with the SALD/SALDVI techniques for depositing silicon nitride. Characteristics of Si₃N₄ fabricated shapes are discussed, including composition, morphology, and electrical properties.

"SALDVI Optimization for the Tetramethylsilane-Silicon Carbide System", J.E. Crocker, K.J. Jakubenas, S. Harrison, L.L. Shaw, and H.L. Marcus, *Proceedings from the 1997 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1997, 489-496. **Abstract:** Selective Area Laser Deposition Vapor Infiltration (SALDVI) of silicon carbide powder infiltrated with silicon carbide deposited from tetramethylsilane (TMS) was studied. The effects of deposition time, temperature, and gas precursor pressure are discussed. The discussion centers on the efforts to properly balance these parameters to produce multi-layered shapes with structural integrity, particularly for use as the matrix material for shapes containing embedded devices. This includes optimizing scan speed, deposition temperature, and gas pressure to maximize infiltration to increase density and layer to layer bonding, and minimize excessive deposition to maintain critical dimensions. Initial powder properties are also optimized to minimize bulk motion in the powder bed during deposition, which was observed and identified as a mechanism that reduces inter-layer bonding.

"Net Shape Functional Parts Using Diode Laser", by T. Manzur, C. Roychoudhuri, P. Dua, F. Hossain, and H.L. Marcus, *Proceedings from the 1997 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1997, 99-114.

"Rapid Prototyping and Solid Free Form Fabrication", by J.G. Conley and H.L. Marcus, *Journal of Manufacturing Science and Engineering*, November, 1997.

"Multiple Material Solid Free-Form Fabrication by Selective Area Laser Deposition" by K. J. Jakubenas, J.M. Sanchez, and H.L. Marcus, *Materials & Design*, 1997.

"Gas-Phase Selective Area Laser Deposition (SALD) Joining of SiC Tubes with SiC Filler Material" by S. Harrison and H.L. Marcus, *Proceedings of the 1998 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1998, 537-542. **Abstract:** The laser-driven, gas phase based SFF technique for joining together ceramic components with ceramic filler material, known as Selective Area Laser Deposition (SALD) Joining, was utilized in fabricating joined silicon carbide structures. Specifically, silicon carbide tubes were 'welded' together by depositing silicon carbide from a gas phase reaction. Two different precursor environments were examined, one a tetramethylsilane/hydrogen mixture and the other composed of methyltrichlorosilane. The quality of the joints were examined by bend tests and hermeticity measurements. In addition, the composition and morphology of the silicon carbide deposit was studied and is discussed here.

"Preparation and Properties of In-Situ Devices Using the SALD and SALDVI Techniques" by J.E. Crocker, L. Sun, L.L. Shaw and H.L. Marcus, *Proceedings of the 1998 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1998, 543-547. **Abstract:** One of the many advantages of the Selective Area Laser Deposition (SALD) and the Selective Area Laser Deposition Vapor Infiltration (SALDVI) is that they can be used to embed in-situ micro-sensors within macro-components. The single-point SiC/C thermocouple sensor embedded within SiC macro-component and electrically insulated with silicon nitride layers has been demonstrated. In many applications, multi-point sensors within a single component are needed, e.g., in monitoring temperature gradient and distribution at different positions. In this paper, the multi-point thermocouple devices are demonstrated. The macro-component is a SiC bulk shape made by infiltrating vapor deposited silicon carbide into a silicon carbide powder bed using the SALDVI

technique. Multiple SiC/C thermocouples are embedded in-situ in the SiC bulk shape using the SALD technique. The transient and steady state responses of the embedded thermocouples are compared to reference thermocouples probing the surfaces of the bulk shape.

"Using SALDVI and SALD with Multi-Material Structures" J.E. Crocker, S. Harrison, L. Sun, L.L. Shaw and H.L. Marcus, *JOM*, **50**, 21-23, December 1998. **Abstract:** Two techniques for solid freeform fabrication using gas precursors and localized laser heating are Selective Area Laser Deposition (SALD) and Selective Area Laser Deposition Vapor Infiltration (SALDVI). The concepts, capabilities, and processing issues of the two techniques are described. An example of a multiple material structure fabricated using SALD and SALDVI illustrates the versatility of these developing processes.

"Gas Phase Solid Free-Form Fabrication and Joining of Ceramics", by K.J. Jakubenas, J.E. Crocker, S. Harrison, L. Sun, L.L. Shaw and H.L. Marcus, *Naval Research Reviews*, July 1998.

"In-Situ Thermocouples in Macro-Components Fabricated Using SALD and SALDVI Techniques: Parts I. Thermochemical Modeling" by L. Sun, K.J. Jakubenas, J.E. Crocker, S. Harrison, L.L. Shaw and H.L. Marcus, *Materials and Manufacturing Processes*, **13**, 859-882, 1998. **Abstract:** To fabricate macro-structural SiC components containing an in-situ SiC/C thermocouple using an integrated SALD and SALDVI technique, thermodynamic analyses on the involved reactant gases have been performed with the CET89 code based on the minimization of the system free energy. The gaseous precursors considered include tetramethylsilane (TMS) and methyltrichlorosilane (MTS) for the deposition of silicon carbide, and methane, ethylene, and acetylene for the deposition of carbon. Reactions between disilane and acetylene and between TMS and ammonia have also been thermodynamically calculated for the deposition of silicon carbide and silicon nitride (for use as an insulation layer between the thermocouple and the matrix), respectively. Based on these analyses, four characteristic temperature zones have been defined for the decomposition of silicon carbide from TMS. A silicon nitride deposition map has been built for the TMS and ammonia system. The deposition temperature range of silicon nitride is found to increase with the total pressure of TMS plus ammonia and the addition of hydrogen, and be affected by the ratio of TMS to ammonia. The addition of hydrogen also introduces a stable silicon carbide and silicon nitride mixture zone that otherwise does not exist. The co-deposition of graphite with silicon carbide and silicon nitride is found in the TMS-containing systems at certain conditions. However, the threshold temperature at which graphite co-deposition occurs can be increased by the addition of hydrogen, thereby eliminating or reducing the graphite co-deposition. Based on these thermodynamic analyses, the gaseous precursors for the deposition of silicon carbide, silicon nitride and carbon have been selected for further experimental evaluation, the result of which is reported in part II of this series.

"In-Situ Thermocouples in Macro-Components Fabricated Using SALD and SALDVI Techniques: Parts II. Evaluation of Processing Parameters" by L. Sun, K.J. Jakubenas, J.E. Crocker, S. Harrison, L.L. Shaw and H.L. Marcus, *Materials and Manufacturing Processes*, **13**, 883-907, 1998. **Abstract:** In order to fabricate well-controlled in situ SiC/C thermocouples embedded within macro-structural SiC components using an integrated selective area laser deposition (SALD) and the selective area laser deposition and vapor infiltration (SALDVI) technique, the major processing parameters affecting the crystal structure, the deposition rate, surface morphology of deposits, and shapes and sizes of the cross section of deposited lines are evaluated. It is found that the growth rate of SiC deposits increases with temperature and tetramethylsilane (TMS) gas pressure over the temperature and pressure range studied. The apparent activation energy for depositing SiC from TMS is 61 kJ/mole in the temperature range from 700 to 1200 °C and independent of the TMS gas pressure ranging from 20 to 60 Torr. The shape and size of the cross section of SiC lines depend strongly on the deposition temperature. XRD examination indicates that the deposition product using a C_2H_2 precursor at 900 °C is crystalline graphite. The crystallinity of Si_3N_4 deposits is affected by the substrate material even though the deposition temperature and other process parameters are the same. These phenomenon have been explained in terms of the growth controlling mechanisms of deposits, the temperature distribution induced by an incident laser beam, and the thermal conductivity of the substrate.

"In-Situ Thermocouples in Macro-Components Fabricated Using SALD and SALDVI Techniques: Parts III. Fabrication and Properties of the SiC/C Thermocouple Device " by L. Sun, K.J. Jakubenas, J.E. Crocker, S. Harrison, L.L. Shaw and H.L. Marcus, *Materials and Manufacturing Processes*, **13**, 909-919, 1998.

"Investigation on Morphology and Microstructure of SALD SiC," L. Sun, J.E. Crocker, L.L. Shaw, and H.L. Marcus, *MRS Symposium Proceedings Series*, Vol. 542, 37-42, 1998. **Abstract:** In this work, the deposition of silicon carbide using a tetramethylsilane (TMS) precursor was investigated. Effects of target temperatures on the morphology and crystal structure of the deposits were examined. It was found that the morphology of the SALD SiC depends strongly on the target temperature. The contour of the cross section of the SiC deposits changes from a triangle to trapezoid to volcano shape and the surface morphology of the deposited lines changes from smooth to rough to porous as the target temperature increases. A critical temperature was found to be about 700 °C to initiate deposition of SiC under the current experimental conditions. X-ray diffraction analyses show that the SALD SiC formed at 1000 °C contains both crystalline and amorphous phases. The results are briefly discussed.

"Gas-Phase Selective Area Laser Deposition (SALD) Joining of SiC", S. Harrison and H.L. Marcus, *Materials and Design*, 20, 147-152 (1999). **Abstract:** The laser-driven, gas-phase based SFF technique for joining together ceramic components with ceramic filler material, known as Selective Area Laser Deposition (SALD) Joining, was utilized in fabricating joined silicon carbide structures. Specifically, silicon carbide tubes were welded together by depositing silicon carbide from a gas phase reaction. A single laser beam deposition setup and a dual laser beam design were investigated. A gas environment of tetramethylsilane and hydrogen served as the deposition precursors. The quality of the joints were examined by bend tests and hermeticity measurements. In addition, the composition and morphology of the silicon carbide deposit was studied and is discussed here.

"Localized CVD and the Ultrafine Grain Structure", J.E. Crocker, L. Sun, S. Harrison, L.L. Shaw, and H.L. Marcus, *Proceedings of TMS Ultrafine Grained Materials Symposium*, Nashville, TN, March 2000, pp. 13-21. **Abstract:** In high rate localized chemical vapor deposition using a laser beam to thermally decompose gas precursors the resulting grain size ranges from the near amorphous to a continuum of ultrafine grain sizes depending on processing parameters. This paper will describe the nature of the grain sizes for various ceramic materials as a function of processing and post-processing conditions. The grain size characterizations were performed using Raman spectroscopy, NMR, TEM, X-ray and other analytic approaches. The results will be described in terms of the various characterization approaches and related to modeling of the processing variables.

"Structural Analysis of Silicon Carbide Deposited by Gas-Phase Selective Area Laser Deposition (SALD)", S. Harrison and H.L. Marcus, *Proceedings of the 1999 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1999. **Abstract:** Silicon carbide deposited by the gas-phase Selective Area Laser Deposition (SALD) process underwent structural analysis in this investigation. The silicon carbide material was locally formed from a gas precursor mixture of tetramethylsilane and hydrogen, at a deposition temperature of approximately 1100 °C and maintained by a closed-loop laser control system. Ground powder samples of the SALD silicon carbide material were examined by Magic Angle Spinning-Nuclear Magnetic Resonance, X-ray Diffraction and Transmission Electron Microscopy. The results from these analytical tools show a significant level of twinning in the SALD SiC material which explains the significant differences between the NMR and X-ray spectra.

"Effect of Hydrogen on Silicon Carbide Deposition from Tetramethylsilane - Raman Scattering Studies", L. Sun, J.E. Crocker, L.L. Shaw, and H.L. Marcus, *Proceedings of the 1999 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1999. **Abstract:** Selective area laser deposition (SALD) is a unique technique for fabricating complex ceramic shapes, tailoring functionally graded structures and embedding in-situ sensors into ceramic parts. In general, high deposition rate is desired. For the case of fabricating in-situ sensors, the chemical composition must also be controlled. Proper shapes and deposition rate using tetramethylsilane (TMS) gas precursor to deposit SiC has been demonstrated in previous studies. However, carbon contamination has been found to be a potential obstacle for the further application of this precursor in sensor-related fabrication. It has been suggested using the thermodynamic calculation that hydrogen has significant effect on the composition of SiC deposits. In this study, therefore, the effect of hydrogen on the SALD SiC will be experimentally evaluated.

"Processing and Characterization of SALDVI Ceramic Structures", J.E. Crocker, L. Sun, H. Ansquer, L.L. Shaw, and H.L. Marcus, *Proceedings of the 1999 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1999. **Abstract:** Selective Area Laser Deposition Vapor Infiltration (SALDVI) ceramic structures and composites are fabricated by the localized chemical vapor infiltration of powder layers. A matrix of vapor deposited ceramic material is selectively deposited from gas precursors into a bed of ceramic powder particles using laser heating. An important aspect of the SALDVI process for building 3-D structures is the depth of penetration of the infiltration zone into the powder layer. The infiltration behavior of vapor deposited silicon carbide from tetramethylsilane gas

was investigated for a range of ceramic powders with different optical, thermal, and physical properties using image analysis. The porosity distribution in the silicon carbide matrix SALDVI structure was found to vary with particle size and particle material. These results will be used to guide experiments on the effect of layer thickness on the microstructure of multiple layer SALDVI composites.

"A SFF Approach Utilizing Condensed Gas Precursors and Pulsed Laser Deposition", E. Geiss and H.L. Marcus, *Proceedings of the 1999 Solid Freeform Fabrication Symposium*, Austin, TX, August, 1999. **Abstract:** Two techniques were studied to direct write diamond-like carbon (DLC) films. The first process employed a pulsed YAG laser to decompose a frozen precursor and deposit thin films directly on SiC and 304 stainless steel. After the initial film is deposited, additional layers may be subsequently condensed and deposited onto the substrate.

"Silicon-29 Solid-State MAS NMR Investigation of Selective Area Laser Deposition Silicon Carbide Material," S. Harrison, X. Xie, K.J. Jakubenas, and H.L. Marcus, *Journal of the American Ceramic Society*, 1999.

"Gas-Phase Solid Freeform Fabrication of SiC Cermets Using SALDVI", J.E. Crocker, L.L. Shaw, and H.L. Marcus, *Proceedings of the 2000 Solid Freeform Fabrication Symposium*, Austin, TX, August, 2000. **Abstract:** Selective Area Laser Deposition Vapor Infiltration (SALDVI) is an experimental solid freeform fabrication (SFF) technique aimed at the direct fabrication of ceramic and ceramic/metal structures and composites. SALDVI uses a layer-by-layer approach in which powders are infiltrated with solid material deposited from gas precursors by chemical vapor deposition (CVD) using laser heating. Experiments have been performed with CO₂ and Nd:YAG lasers using the silicon carbide forming gas precursor Si(CH₃)₄ and Cu, Mo, and Ni metal powders. The microstructure of the resulting SiC/metal cermets was investigated in relation to the processing history. In some cases, the formation of intermetallic silicide phases was observed.

"Gas Phase Solid Freeform Fabrication of SALDVI of SiC Cermets", J.E. Crocker, L. Shaw, H.L. Marcus, *MRS Proceedings*, 2000, **Abstract:** In this work, the solid freeform fabrication of cermets was explored. Using a laser-based approach, SiC was deposited by chemical vapor deposition from tetramethylsilane gas into powder layers of Cu, Mo, or Ni. The resulting structures were examined to observe the extent of reaction between the metal powders and the vapor deposited SiC. Silicide formation was observed, most readily with the Ni powder. The thermal expansion of the metals compared to that of the vapor deposited SiC affected the interfacial stresses generated in the cermets during fabrication.

"Finite Element Analysis of the SALDVI Process", K. Dai, J. Crocker, L. Shaw, and H. Marcus, *Proceedings of the 2000 Solid Freeform Fabrication Symposium*, Austin, TX, August, 2000. **Abstract:** Selective Area Laser Deposition Vapor Infiltration (SALDVI) is a developing solid freeform fabrication (SFF) technique aimed at the direct fabrication of ceramic and ceramic/metal structures and composites. SALDVI uses a layer-by-layer approach in which layers of powder are densified with solid material deposited from gas precursors by chemical vapor deposition (CVD) using laser heating. In this work, we have performed numerical simulation using the ANSYS code with 3-dimensional coupled field elements to calculate the temperature field and the part geometry resulting from the SALDVI process. The effects of the powder and vapor deposited material properties on the temperature distribution and the part geometry have been investigated. The result from the numerical simulation is found to be consistent with those obtained from experiments performed using the silicon carbide forming gas precursor Si(CH₃)₄ and SiC powder particles.

"SALDVI of SiC Into Metal and Ceramic Powders", J.E. Crocker, H. Wei, L.L. Shaw, and H.L. Marcus, *Proceedings of the 2001 Solid Freeform Fabrication Symposium*, Austin, TX, August, 2001. **Abstract:** Selective Area Laser Deposition Vapor Infiltration (SALDVI) is the SFF technique using gas phase precursors to locally infiltrate a powder bed into a desired shape. Experiments were performed with a CO₂ laser and the silicon carbide forming gas precursor Si(CH₃)₄. This paper will report on the microstructural aspects of SiC into a variety of metal and ceramic powders including Mo, SiC, ZrO₂, and WC.

"Modeling of Selective Area Laser Deposition Vapor Infiltration (SALDVI) of Silicon Carbide", K. Dai, J. Crocker, L. Shaw and H. Marcus, *Proceedings of the 2001 Solid Freeform Fabrication Symposium*, Austin, TX, August, 2001. **Abstract:** Selective Area Laser Deposition Vapor Infiltration (SALDVI) is a developing solid freeform fabrication (SFF) technique in which porous layers of powder are densified by infiltrating the pore spaces with solid

material deposited from a gas precursor during laser heating. A 3D finite element model was developed that simulates SALDVI of silicon carbide. The model predicts the laser input power and the distribution of vapor deposited SiC within the powder bed as well as on the surface of the powder bed (SALD). The model includes closed-loop control of the laser power to achieve a desired target processing temperature on the top surface of the powder bed. This model considers a moving Gaussian distribution laser beam, temperature- and porous-dependent thermal conductivity, specific heat and temperature-dependent deposition rate. The simulation results agree fairly well with experimental data for simple geometries and offer guidelines for further experimental studies of the SALDVI process.

"Spot Joining of Si_3N_4 and SiC Ceramics Using Selective Area Laser Deposition (SALD) Technique", I.M. Ghayad, E. Geiss, J.E. Crocker, and H.L. Marcus, *Proceedings of the 2001 Solid Freeform Fabrication Symposium*, Austin, TX, August, 2001. **Abstract:** A new, promising manufacturing path involves a gas-phase decomposition approach, known as Selective Area Laser Deposition (SALD) Joining. SALD is a gas-phase Solid Freeform Fabrication (SFF) process in which a specific gas mixture decomposes either thermally or photolytically from the energy input of a laser beam to form a solid reaction product. The chemical process is similar to Chemical Vapor Deposition (CVD) but the product is selectively deposited locally under the laser spot, which can be scanned, and therefore controlled. The present paper focuses on deposition of silicon nitride or silicon carbide filler materials to spot join silicon nitride and silicon carbide ceramic materials. Chemical and structural characterization of joints were performed.

"Powder Effects in SiC Matrix Layered Structures Fabricated Using SALDVI", J.E. Crocker, L.L. Shaw, and H.L. Marcus, to appear in *Journal of Materials Science*, 2002. **Abstract:** Silicon carbide has been deposited by laser-induced chemical vapor infiltration from the gas precursor tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, into loosely packed powder layers of SiC, $\text{ZrO}_2\text{-Y}_2\text{O}_3$, or Mo. The goal is to produce dense layered structures of arbitrary shape by computer controlled laser scanning where the pore spaces between the powder particles are filled with solid material deposited from the gas phase using the Selective Area Laser Deposition Vapor Infiltration (SALDVI) process. Layered samples were fabricated for each powder material using both single line (bar) and multiple line (slab) laser scan patterns and 10 Torr $\text{Si}(\text{CH}_3)_4$, 2.5 $\mu\text{m/s}$ scan speed, 1000 $^\circ\text{C}$ target temperature, and 120 μm layer thickness. Samples of SiC and $\text{ZrO}_2\text{-Y}_2\text{O}_3$ are prone to surface cracking in the bar geometry, and cracking and delamination of layers in the slab geometry. Samples fabricated with Mo powder have no cracks or delamination defects in either bar or slab geometry as well as a better surface appearance.